



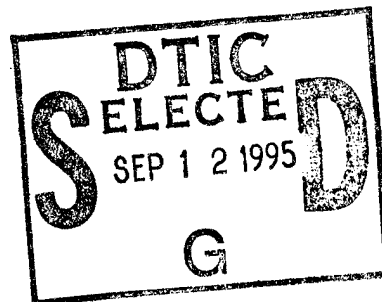
EDGEWOOD

RESEARCH, DEVELOPMENT & ENGINEERING CENTER

U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-TR-249

**TSA-CATOX FOR AIR PURIFICATION AND
PURGE EFFLUENT DETOXIFICATION**



Roy S. Brown

GUILD ASSOCIATES, INC.
Hilliard, OH 43026

David K. Friday

GUILD ASSOCIATES, INC.
Baltimore, MD 21236

David E. Tevault

RESEARCH AND TECHNOLOGY DIRECTORATE

June 1995

19950911 005

Approved for public release; distribution is unlimited.



Aberdeen Proving Ground, MD 21010-5423

DTIC QUALITY INSPECTED 6

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1995 June		3. REPORT TYPE AND DATES COVERED Final, 94 Jun - 95 Jan
4. TITLE AND SUBTITLE TSA-CatOx for Air Purification and Purge Effluent Detoxification			5. FUNDING NUMBERS PR-1O162622A553	
6. AUTHOR(S) Brown, Roy S.; David K. Friday (Guild Associates, Inc.); Tevault, David E. (ERDEC)				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Guild Associates Inc., 4089 N. Leap Rd, Hilliard, OH 43026 Guild Associates Inc., 5022 Campbell Blvd, Suites J and K, Baltimore, MD 21236 DIR, ERDEC, ATTN: SCBRD-RTE, APG, MD 21010-5423			8. PERFORMING ORGANIZATION REPORT NUMBER ERDEC-TR-249	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The removal of toxic chemical vapors from air and the subsequent treatment of those chemicals is an ever-growing environmental problem. A unique system has been developed which is capable of removing toxic chemical vapors from air and detoxifying these chemical vapors, <i>in situ</i> . Temperature Swing Adsorption (TSA) is used to continuously remove the toxic constituents from the incoming air stream using a two-bed cyclic operation. During the desorption (purge) step in the TSA cycle, a hot, concentrated effluent is generated which is fed to a catalyst reactor to decompose the toxic vapors. The design and operation of the TSA makes the system unique and is the focus of this work. During the purge step, energy is introduced into the system by heating the adsorbent directly. This permits heating without flow, which is not possible using the traditional TSA methods of purge gas or steam regeneration. An important consequence of this capability is that purge-step, vapor-phase concentrations may be increased by orders of magnitude over the feed concentrations. Parameters such as the power input and the purge flow rate may be adjusted to achieve the desired purge effluent quality, while maintaining the required product air purity. These design improvements allow the TSA to (1) satisfy even the most stringent air quality requirements and (2) generate a TSA purge effluent (both concentration and flow rate) tailored to optimize catalyst system performance.				
14. SUBJECT TERMS Air purification Catalytic oxidation Regenerative filtration			15. NUMBER OF PAGES 20	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

Blank

PREFACE

The work described in this report was authorized under Project No. 1O162622A553, CB Defense/General Investigation. This work was started in June 1994 and completed in January 1995.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for release to the public. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Accession For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification _____	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Blank

CONTENTS

1.	INTRODUCTION	1
2.	MATHEMATICAL MODEL	2
3.	EXPERIMENTS	2
4.	CONCLUSIONS	5
5.	LITERATURE CITED	5

FIGURES

1.	TSA-CatOx System Schematic	6
2.	TSA Bed Resistive Heating Configuration	7
3.	Purge Effluent Partial Pressures for Experiments 1 and 2	8
4.	In-Bed Temperature Data for Experiment 1 and Experiment 2	9
5.	R-123 BPL Activated Carbon Isotherm Data (symbols) with the Best Fit 5-Parameter Virial Equation (lines)	10
6.	Purge Effluent Partial Pressures with Time	11
7.	In-bed Temperatures for Experiment 2	12
8.	Design Model In-bed Partial Pressure Profiles for 3-Step Feed Simulation	13
9.	Design Model Purge Effluent Temperatures and Partial Pressures for 3-Step Feed Simulation	14

TSA-CATOX FOR AIR PURIFICATION AND PURGE EFFLUENT DETOXIFICATION

1. INTRODUCTION

An important and ever-growing problem is removing volatile organic compounds (VOC's) from effluent air streams and the subsequent post-processing (recovery for reuse or destruction) of these VOC's in an energy efficient and environmentally acceptable manner. The standard approach used in most applications is a single-pass carbon filter. In most cases this would appear to be the simplest and most cost-effective means of treating the problem. However, there are significant problems with this approach. To insure that performance specifications are met, single-pass filters must be designed to remain on-stream for at least several days of operation. If no method of monitoring the effluent concentration of contaminate(s) is provided, then filters typically must be sized for the worst case situation. This results in filters which are excessively large, thereby increasing both capital costs and waste generation.

A system capable of purifying air and treating the chemical waste at the point of production is shown in Figure 1. Temperature Swing Adsorption (TSA) is used to remove chemical vapors from air and generate a concentrated purge effluent stream. A catalytic (Cat-Ox) reactor is used to subsequently decompose these vapors. A purge air heater is not required for the TSA operation because a relatively new, more efficient method is employed. Using an activated carbon adsorbent, an electrical potential is induced across the bed. Since carbon can conduct electricity and has a measurable resistance, electrical energy supplied to the bed is converted to resistive heat. Most importantly, the energy introduced into the system goes directly to the point where it is required, the adsorbent, as opposed to traditional TSA purge gas techniques which require a heat transfer step. Consequently, the flow rate of purge gas is no longer important in determining the heating rate, thus the heating time and cycle time may be proportionately reduced.

The regeneration step in the TSA cycle is typically composed of a heating and a cooling stage. Invariably the regeneration step is the time limiting step of the TSA cycle. It is also the most complex and the least understood. Friday and LeVan (1, 2) performed a theoretical analysis of the purge step for two systems, (1) benzene on activated carbon and (3) water on 4-A molecular sieve. They also conducted an experimental study of the regeneration of an activated carbon bed with adsorbed octane using a hot nitrogen purge (4) and compared measured data with model results. However, their analysis did not include mass transfer resistances which could be significant for complete VOC removal. Shoofs (5) has studied the behavior of the regeneration step of a TSA process to purify ammonia synthesis make-up gas. He reports that monitoring temperature behavior at the exit and within the beds can allow one to estimate the effectiveness of the desorption step. Some qualitative information regarding the magnitude of concentrations within the bed is also obtained.

In-bed resistive heating was suggested by Petkovska et al. (5). In their experiments, activated carbon cloth was placed between two electrodes. Trichloroethane was used as the test chemical. Regeneration experiments were

performed and the following conclusions about direct electrical heating were reached: (1) it is both interesting and applicable, (2) it is rapid, and (3) it is superior to conventional heating methods from an energy point of view.

2. MATHEMATICAL MODEL

The only way to estimate the performance improvements in the TSA system is by using a mathematical model. The basis of the simulation is given by the material and energy balances as described below. A full discussion of the assumptions used to develop the material and energy balances along with the complete list of parameter definitions is given by Friday and LeVan (1).

Material balance

$$\rho_b \frac{\partial q}{\partial t} + \frac{\partial(\epsilon v c)}{\partial z} = 0 \quad (1)$$

Energy Balance

$$\rho_b \frac{\partial h_s}{\partial t} + \frac{\partial(\epsilon v \rho_f h_f)}{\partial z} = \text{Power Density} \quad (2)$$

The power density is expressed as J/(s m³). The mathematical model also includes an internal particle mass transfer resistance, Equation (3), and an external particle heat transfer resistance, Equation (4).

$$\rho_b \frac{\partial q}{\partial t} = k_p a (q^* - q) \quad (3)$$

$$\rho_b \frac{\partial T_s}{\partial t} = h a (T_f - T_s) \quad (4)$$

q^* is the equilibrium adsorbed-phase concentration, T_f is the fluid-phase temperature, T_s is the solid-phase (particle) temperature, $k_p a$ is the mass transfer rate constant and $h a$ is the heat transfer rate constant.

3. EXPERIMENTS

The main purpose of this paper is to demonstrate the capability of the TSA system not only to purify air streams, but to provide a mechanism for more efficient downstream processing of the chemical vapors of interest. The most important characteristic of the TSA operation is the concentration increase achieved during the purge step. Two experiments are performed which demonstrate both the increase in concentration and the flexibility the system has to control the purge effluent concentration profile. The test chemical is 1,1 dichloro, 2,2,2 trifluoroethane (R-123) and the adsorbent is 12x30 mesh BPL carbon manufactured by Calgon Corporation. The most important feature of the experimental system is the in-bed heating configuration depicted in Figure 2. For both experiments, the voltage is held constant at 26V. The bed depth is 50 cm, the bed diameter is 33 cm and the mass of

adsorbent is 22.5 kg. In-bed temperatures are measured using Resistance Temperature Detectors (RTD's) approximately 6.5 cm from each end of the bed. Experiments are compared with mathematical model results to better understand the purge step temperature and concentration behavior.

The feed-step procedure used for both experiments is the same. A clean bed is partially saturated with chemical by feeding 500 ppm (0.38 torr) of R-123 at 100 SCFM for 4 hours. Based on the equilibrium loading for R-123 of 0.182 g/g at 500 ppm and 300 K, this results in the bed being about 1/2 filled with adsorbed chemical. After the 4-hour adsorption step, two different purge steps are employed. For Experiment 1, the purge step consists of 30 minutes of power input at 1.77 kW with no purge flow. The purge flow rate of 15 Standard Cubic Feet per Minute (SCFM) is not initiated until the power is turned off (30 minutes). For Experiment 2, the purge step consists of 15 minutes of power input at 1.65 kW with no purge flow, followed by 15 minutes of power input at 1.65 kW with 15 SCFM purge flow. After 30 minutes the power is turned off while the purge flow continues. For both experiments the purge flow direction is counter-current to the feed flow direction.

Shown in Figure 3 are the purge effluent partial pressure profiles for both experiments. Both experiments show that the purge effluent partial pressure is increased by one to two orders of magnitude over the feed step partial pressure. In addition, these results demonstrate that heating with no flow provides another level of capability to control the purge effluent partial pressure with time. This can be particularly valuable for optimizing a downstream Cat-Ox reactor. Shown in Figure 4 are the in-bed temperatures for both experiments. These results demonstrate the differences in temperature achieved if heating is performed with and without flow. For example, the temperature at the purge outlet probe in Experiment 1 is about 40 K higher than in Experiment 2 at 30 minutes. The temperature behavior of the purge inlet is also different. When the purge flow is started at 15 minutes in Experiment 2, the temperature at the purge inlet rises for about five minutes, then drops as the purge gas cools the bed. The temperature for Experiment 1 however continues to rise reaching a temperature more than 40 K greater than in Experiment 2. The second rise in the in-bed temperatures near the purge outlet for each experiment result from hotter regions of the bed upstream of the probe. This may have been caused by the differences in bed resistance when material is adsorbed versus the bed resistance when the adsorbent is clean.

To further understand the behavior of the system, the experimental results are compared to the mathematical calculations. The mathematical model results are obtained using $D_E = 2.0 \times 10^{-6} \text{ cm}^2/\text{s}$ and a particle diameter (d_p) of 0.15 cm in the following expression for $k_p a$.

$$k_p a = \frac{60 D_E}{d_p^2} \quad (5)$$

The heat transfer coefficient, h_a , was calculated using standard engineering correlations for the Prandtl and Nusselt numbers with a thermal conductivity of 0.0216 J/(s m K) and a particle heat transfer area per mass of adsorbent of 6.96 m²/kg. Adsorption equilibria for R-123 on BPL activated carbon was measured

using a closed-loop isotherm system described in detail by Mahle et al. (9). These data are shown in Figure 5 correlated using the following five-parameter virial expression,

$$\ln(p) = \ln(q) + K_0 + \frac{K_1}{T} + \frac{B_1 q}{T} + \frac{C_1 q^2}{T} + \frac{D_1 q^3}{T} \quad (6)$$

where q is expressed in g adsorbate per g adsorbent and p in torr. Parameter values obtained from a least squares best fit of $\ln(p)$ are $K_0 = 20.240$, $K_1 = -7134.5$, $B_1 = 13594$, $C_1 = -39117$, and $D_1 = 45762$.

Shown in Figure 6 are the purge effluent partial pressure profiles for Experiment 2 compared to the model results. The model seems to be reasonably close initially, but the model predicts a much more rapid drop in the effluent partial pressure than is measured. This discrepancy may be explained by examining the in-bed temperature results for Experiment 2 shown in Figure 7. The predicted temperatures for the purge inlet and the measured temperatures for the purge inlet are in reasonable agreement. However, the additional rise in the measured purge outlet temperature at about 40 to 50 minutes is not accounted for in the model. This is the reason the measured purge effluent partial pressure remains fairly constant at an elevated level. More work to identify the mechanism for the hotter upstream temperatures is required.

The design model was used to examine the purge step behavior of the TSA system with a more realistic feed concentration profile. Using the same bed dimensions and the same adsorbate adsorbent system, a 3-part feed was introduced. The feed concentration was 500 ppm (0.38 torr) for 2 hours, followed by 0 ppm for 2 hours and finally 50 ppm (0.038 torr) for 2 hours. The purge step was the same as in Experiment 1, 30 minutes of heating with no flow, followed by 15 SCFM purge flow. Shown in Figure 8 are the in-bed partial pressures during the heating stage of the purge step. The bed profile at 0 minutes shows the condition of the bed at the conclusion of the 3-part feed step. Although there is a noticeable drop in the partial pressure at about $z/L = 0.1$, the 3-part feed step has been smeared considerably. The maximum partial pressure in the bed is about 0.06 torr (6 times less than the 0.38 torr feed) and it exists near $z/L = 0.6$. When the potential is applied the partial pressures rise by more than 2 orders of magnitude. At the end of the heating step the in-bed profiles are nearly uniform. Figure 9 shows the effluent partial pressures and temperatures starting at 30 minutes when the 15 SCFM purge flow begins. Although the concentration drops continually from a high value of about 25 torr, it remains above 0.38 torr until about 60 minutes and above 0.038 torr for more than 80 minutes. The temperatures are also more than 50 K above ambient until about 70 minutes into the purge step.

4. CONCLUSIONS

The TSA system provides a mechanism for more efficient downstream processing by increasing the concentration and reducing the flow rate of a contaminated air stream. In-bed resistive heating allows the purge effluent concentration to be tailored to optimize a downstream process, e.g., Cat-Ox. The mathematical model results demonstrate that the TSA system is relatively insensitive to wide variations in feed concentrations.

5. LITERATURE CITED

1. D. K. Friday and M. D. LeVan, "Hot Purge Gas Regeneration of Adsorption Beds with Solute Condensation: Experimental Studies," *AIChE J.*, **31**, 1322 (1985).
2. Friday, D.K and LeVan, M.D., "Thermal Regeneration of Adsorption Beds. Equilibrium Theory for Solute Condensation," *AIChE J.*, **30**, 697 (1984).
3. Friday, D.K and LeVan, M.D., "Solute Condensation in Adsorption Beds During Thermal Regeneration," *AIChE J.*, **28**, 86 (1982).
4. Schoofs, G.R., "Operation of Adsorbers for Purifying Ammonia Synthesis Make-Up Gas," *Ind. Eng. Chem. Res.*, **32**, 613 (1993).
5. Petkovska, M., Tondeur, D., Grevillot, G., Granger, J., and Mitrovic, M., "Temperature-Swing Gas Separation with Electrochemical Desorption Step," *Sep. Sci. and Tech.*, **26**, 425 (1991).
6. Mahle, J., Beuttner, L. and Friday, D.K., "Measurement and Correlation of the Adsorption Equilibria of Refrigerant Vapors on Activated Carbon," *Ind. Eng. Chem. Res.*, **33**, 346-354 (1994).

Figure 1.

TSA-CatOx System Schematic

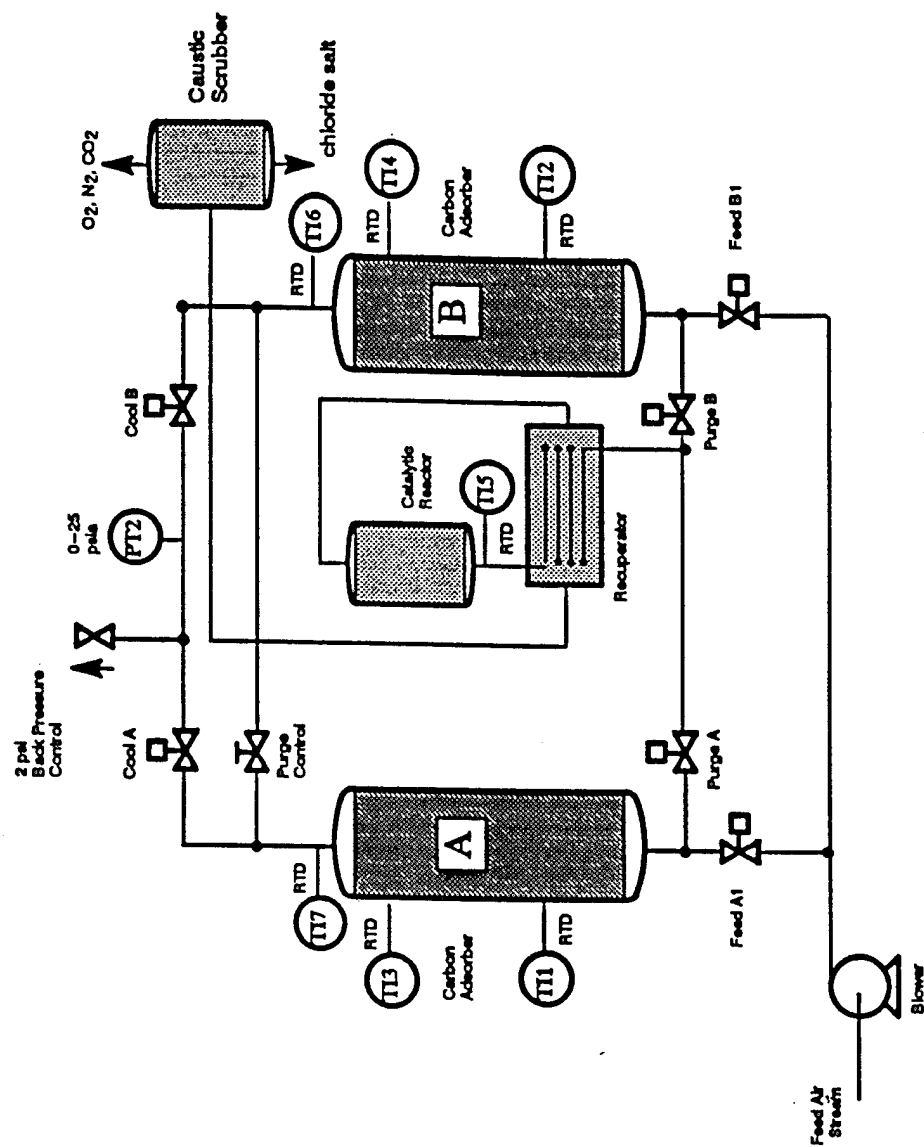


Figure 2.

TSA Bed Resistive Heating Configuration

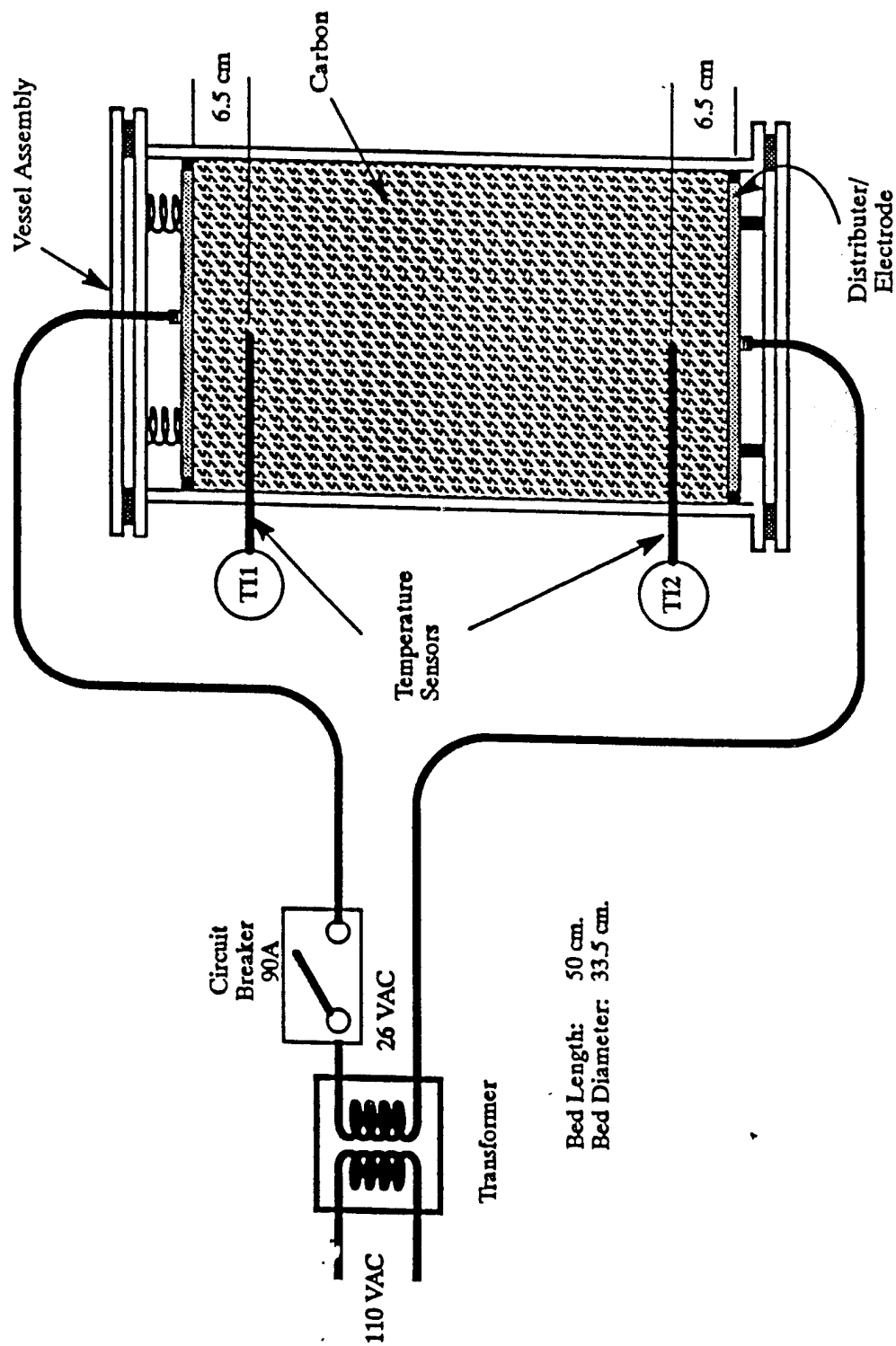


Figure 3. Purge Effluent Partial Pressures for Experiments 1 and 2

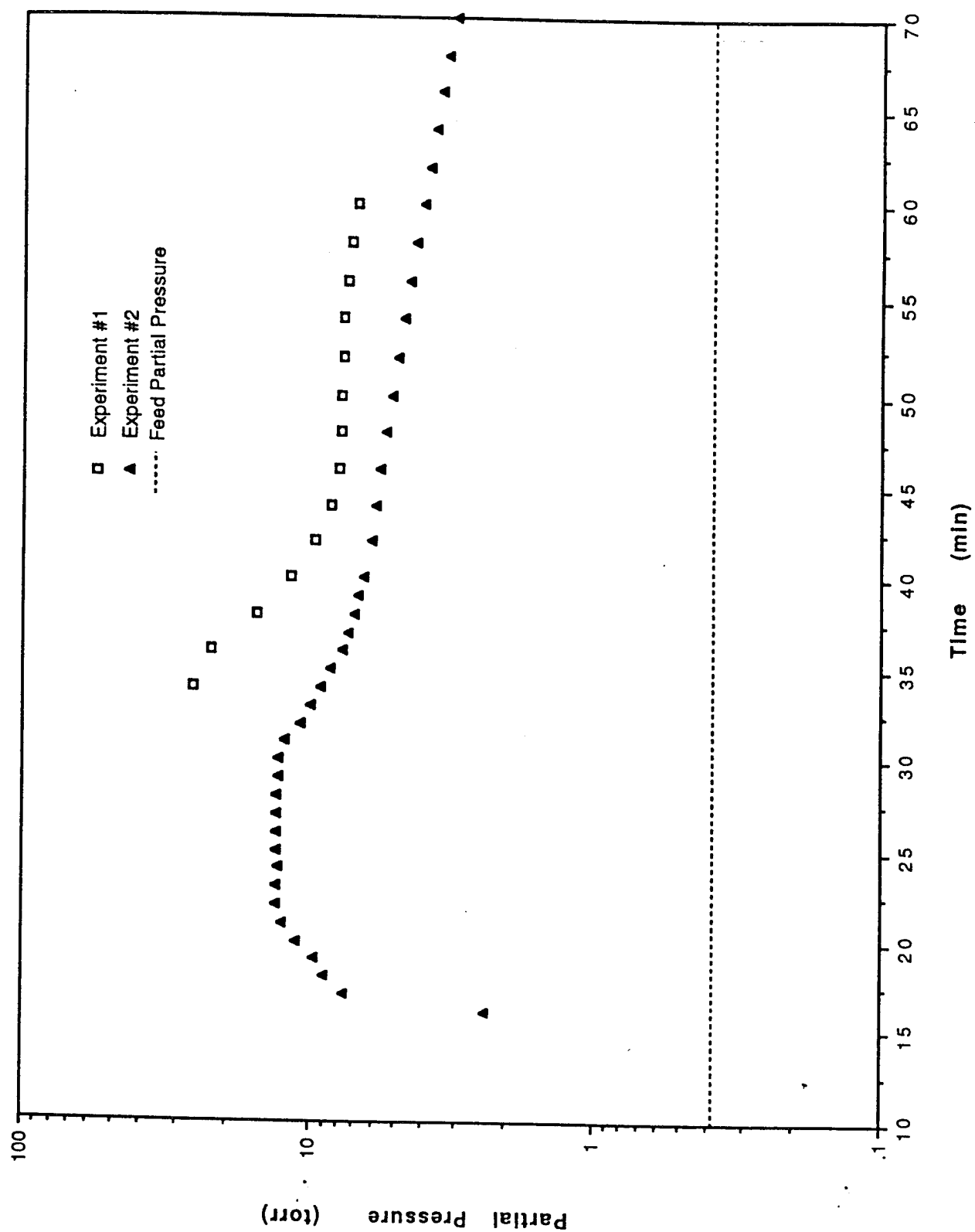


Figure 4. In-bed Temperature Data for Experiment 1 and Experiment 2

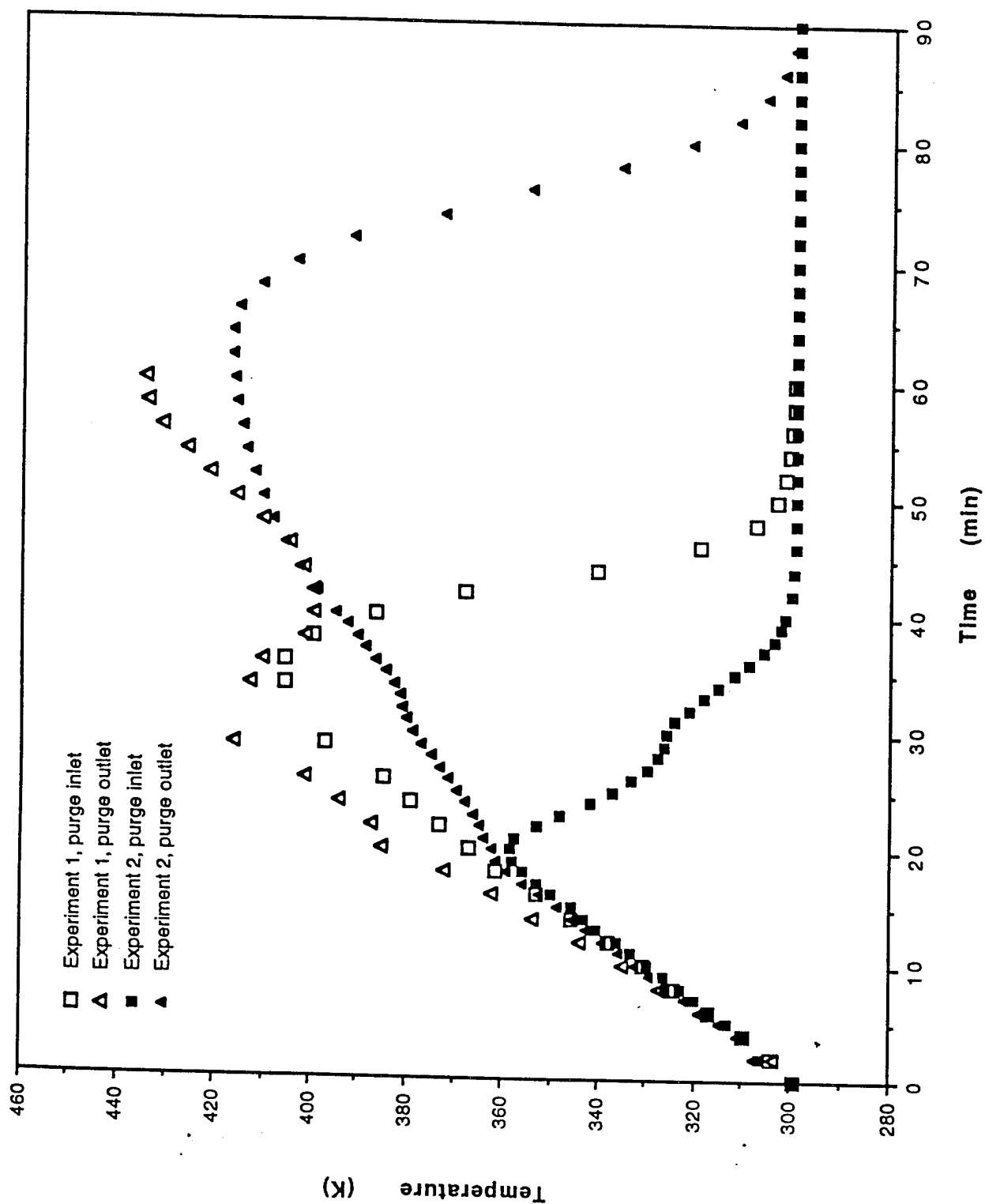


Figure 5. R-123 on BPL Activated Carbon Isotherm Data (symbols)
with the Best Fit 5-parameter Virial Equation (lines)

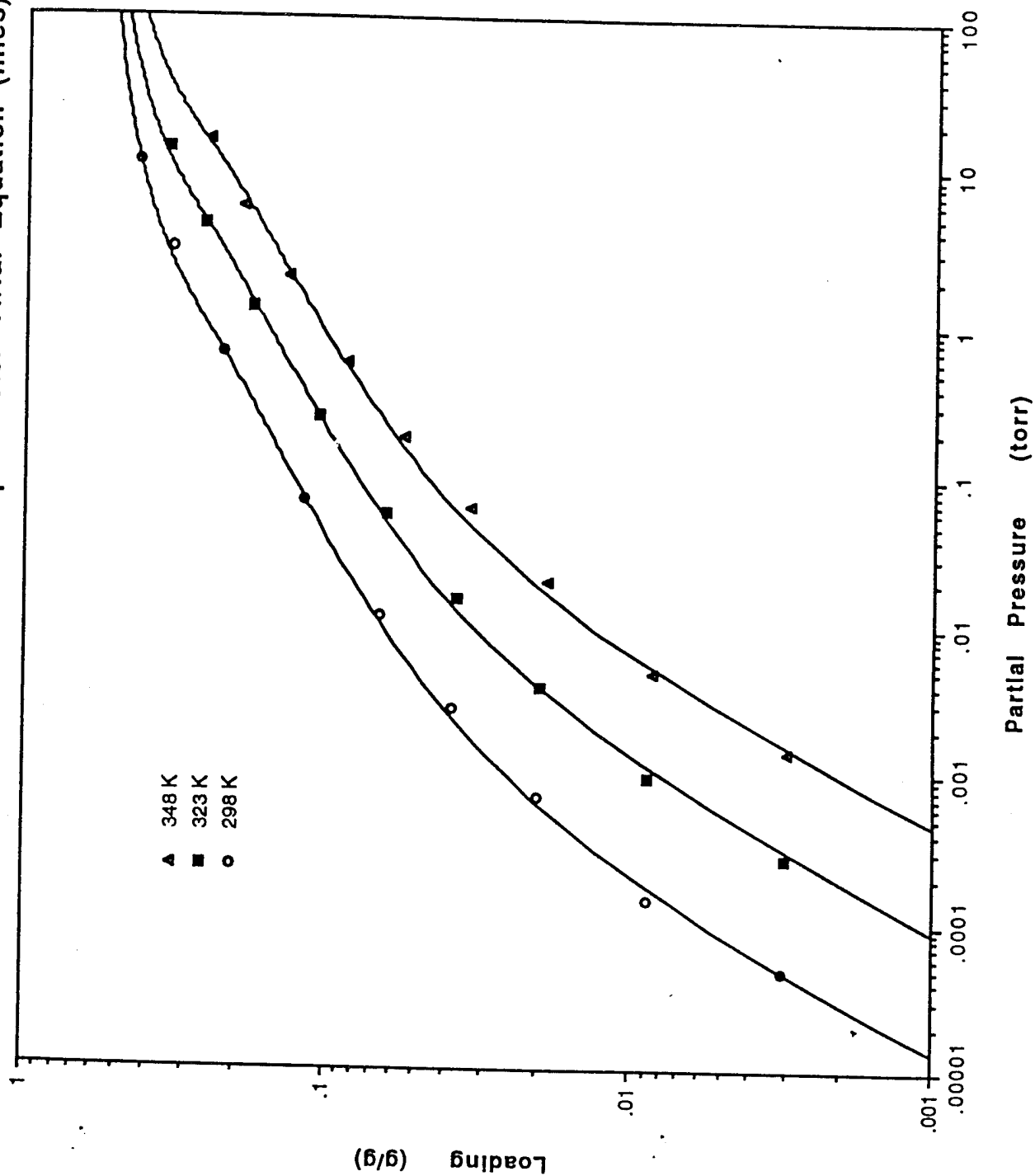


Figure 6. Purge Effluent Partial Pressures with Time.
Model vs Data for Experiment #2

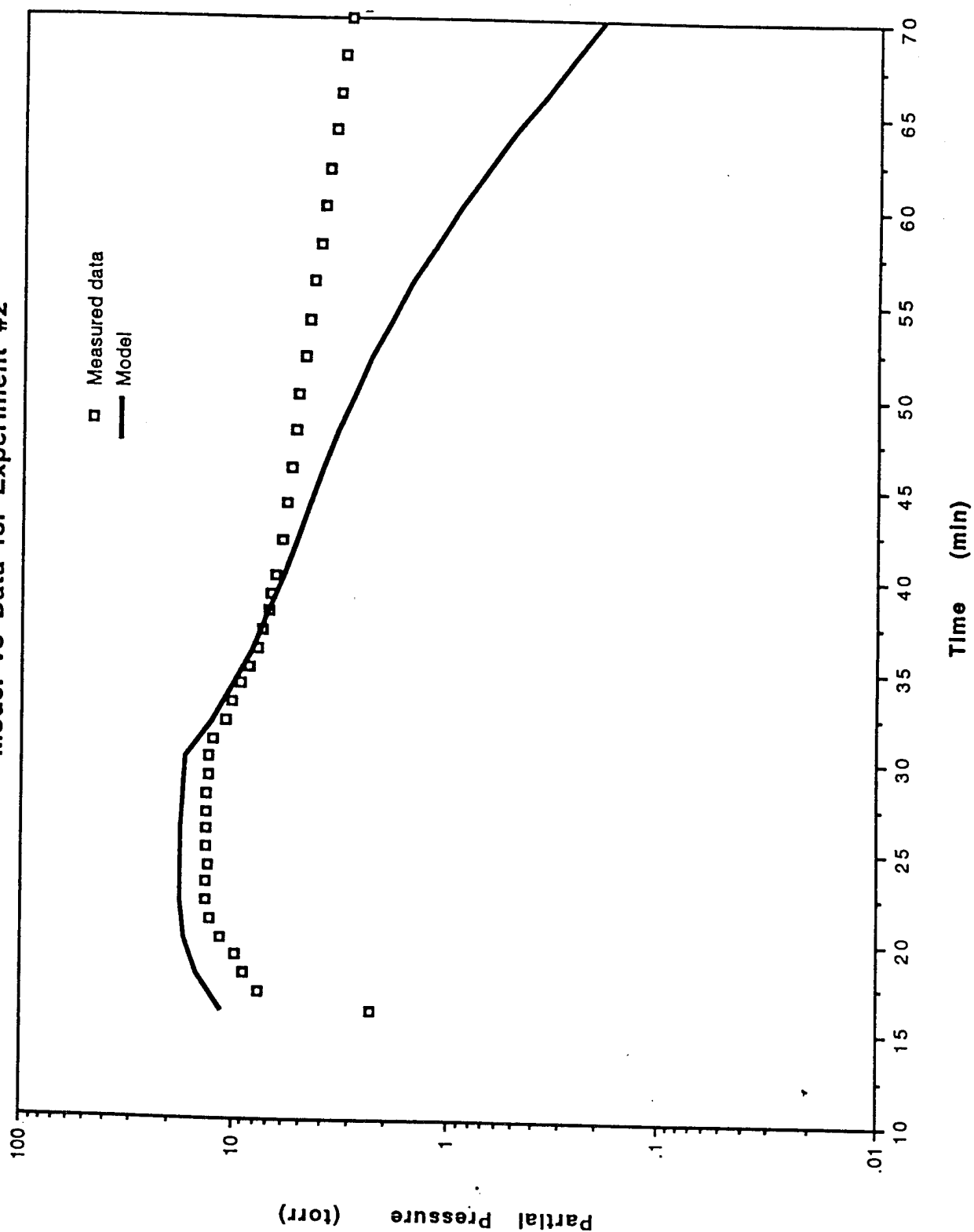


Figure 7. In-bed Temperatures for Experiment 2.
Model Results vs Measured Data

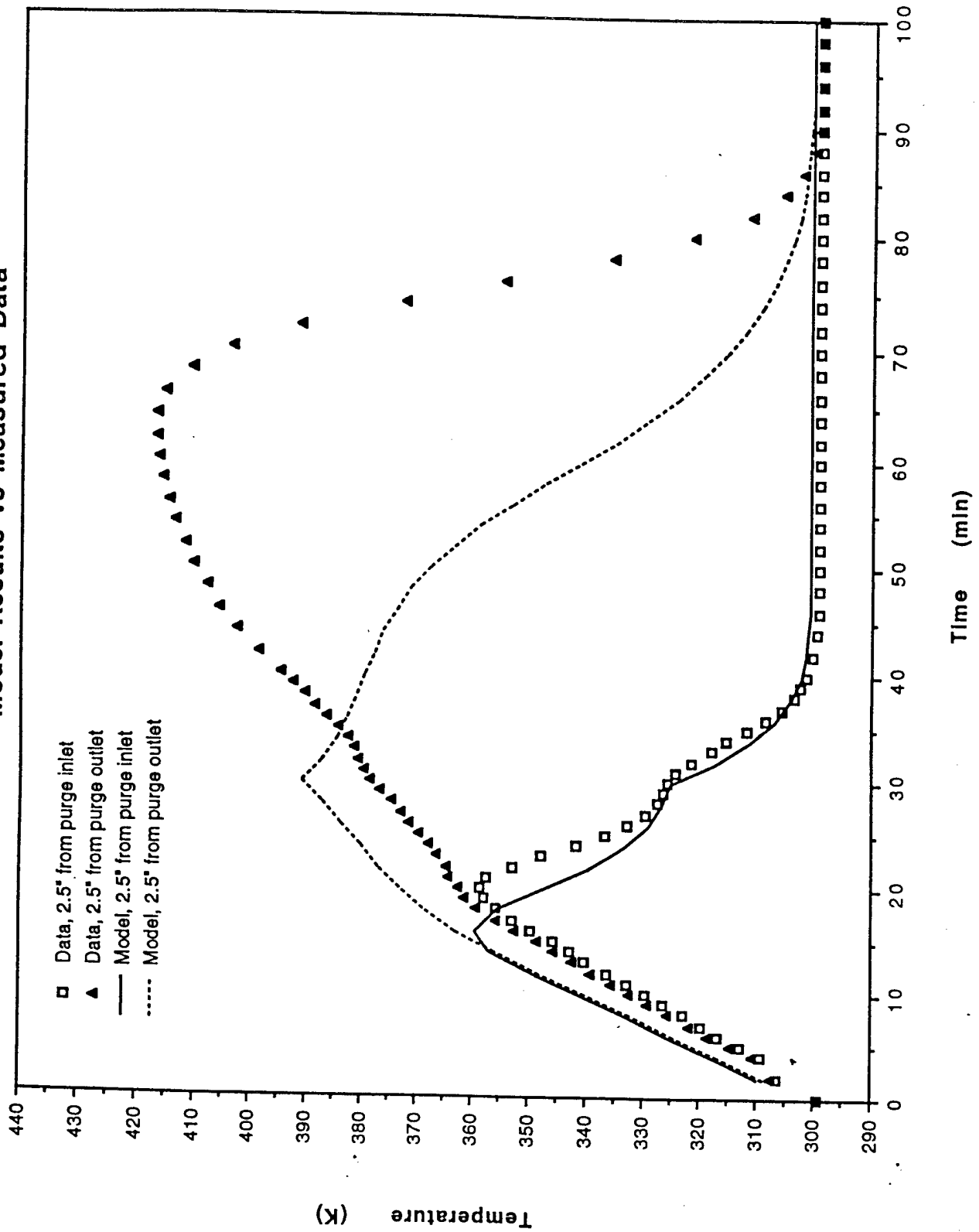


Figure 8. Design Model In-bed Partial Pressure Profiles for 3-step Feed Simulation. 0, 15, and 30 Minutes Into Purge Step

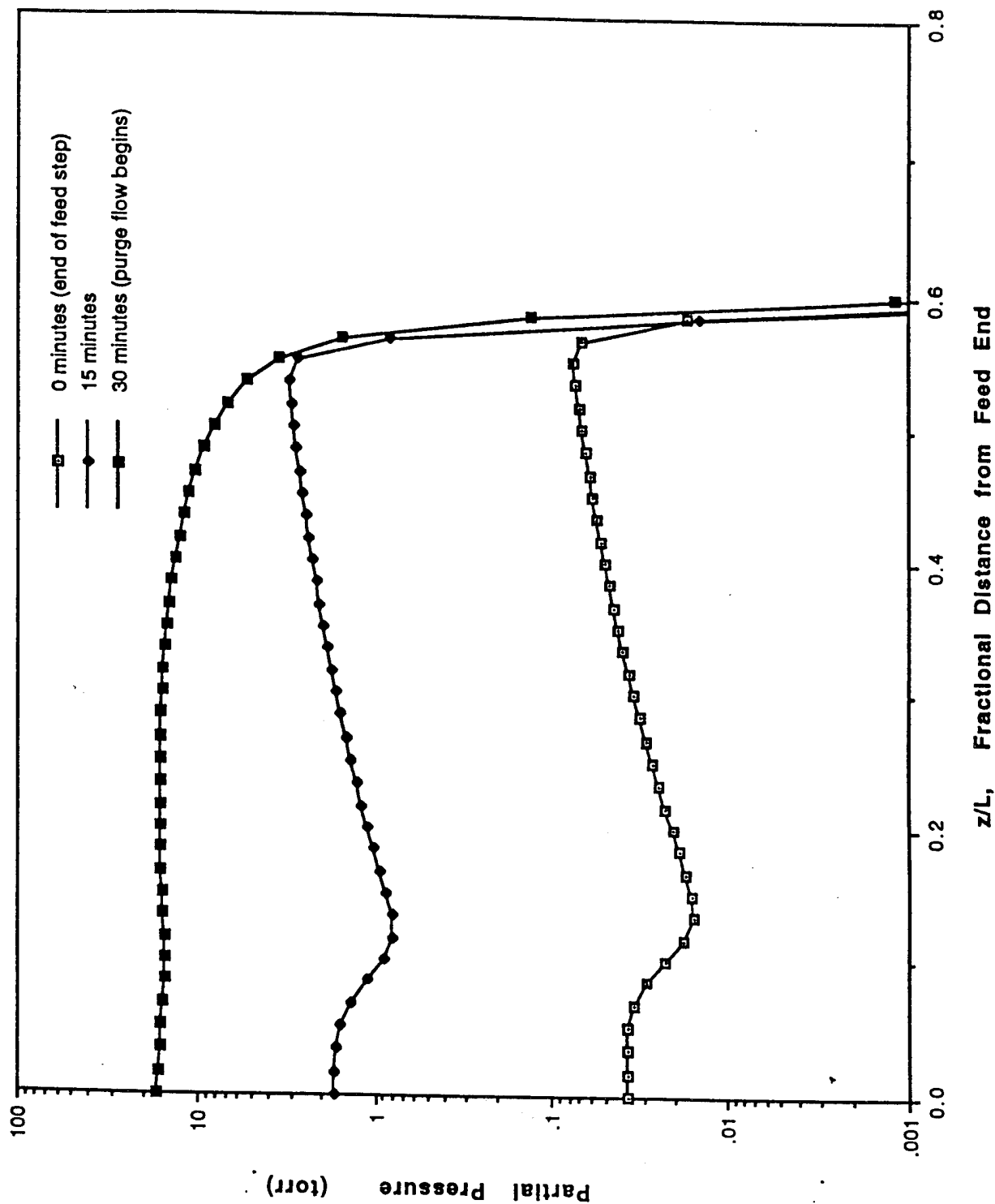


Figure 9. Design Model Purge Effluent Temperatures and Partial Pressures for 3-step Feed Simulation

